Monomolecular Layers of New Materials and Phases

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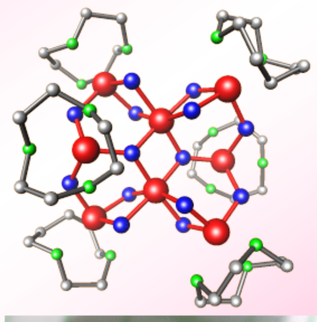
Motivation: **Molecule-scale and molecular sciences are fueling a fascinating expansion of our understanding of materials and are now providing frequent significant breakthroughs at laboratories worldwide. Pure organic superconductors, wires, transistors, switches, and Lasers are a few recent examples. More discoveries are eagerly anticipated due to the inherent quantum nature of the nanometer scale. Using many of the existing tools and areas of expertise at Ames Laboratory, it is possible to contribute to this promising global effort.**

Implementation: **At its inception, this work envisioned the formation of an exploratory *multidisciplinary research effort*, from synthesis to property measurement and analysis, in *nanoscale condensed matter physics* on *new materials and phases*. The design followed the central flowchart as a template. The outlying plates highlight the proof of concept steps successfully accomplished to realize this vision.**

Ames Laboratory

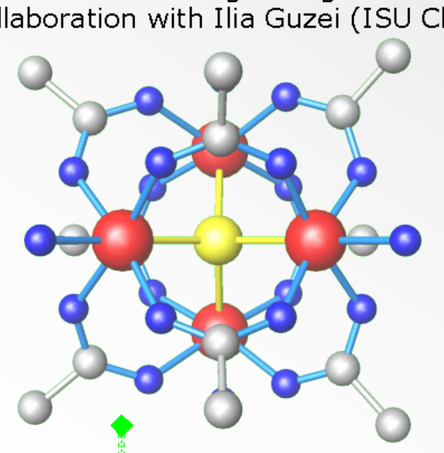
Materials Synthesis

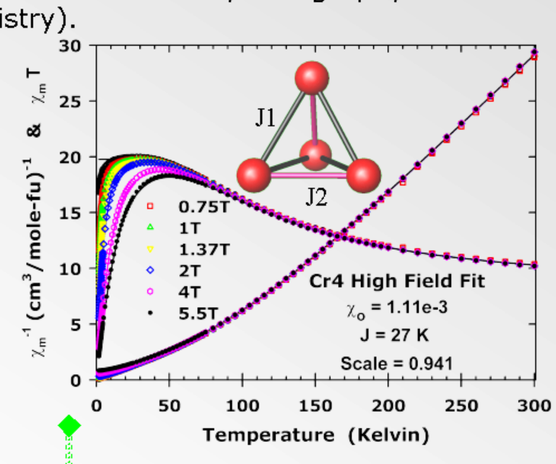
One of the first new materials to come out of the **synthesis** lab was Fe8 (aka $[Fe_8(1,4,7\text{-}C_6H_{15}N_3)_6(OH)_{12}O_2]Br_8 \bullet 8H_2O$ phase II). Fe8 has eight Fe(V) (s =5/2) ions which are almost coplanar. There are 5 Fe-Fe distances of 3.05Å and 8 Fe-Fe distances of 3.45Å. The mixed ground state is reported to be S =10. The system has several exchange coupling constants J ranging from 150K to 25K but they are not well known. There is an anisotropy barrier of ≈ 30K and the molecule exhibits quantum tunneling of the total magnetic spin between degenerate magnetic levels.



Bulk Characterization and Physics

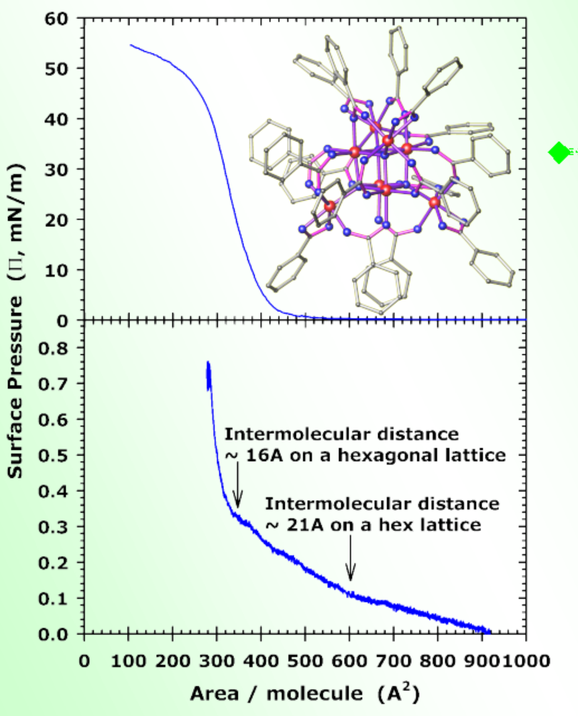
Bulk materials are readily characterized by **crystallography** and **magnetization**. The structure and magnetization of Cr4 (aka $[Cr_4S(O_2CCH_3)_8(H_2O)_4](NO_3)_2H_2O$) is shown below. Cr4 has ferromagnetic intracluster exchange interaction of J ≈ 27 K and a Curie-Weiss Θ = -0.4K. The four Cr(III) ions (s = 3/2) form an almost perfect tetrahedron with Cr-Cr distances of 3.7 to 3.9Å. The cluster ground state is ferromagnetic with S_{Tot} = 6. Very weak intercluster (dipolar) interactions yield an overall antiferromagnetic ground state in the bulk. Crystallography work done in collaboration with Ilia Guzei (ISU Chemistry).





Molecular Monolayers

The **Langmuir-Blodgett** technique is one of several methods used to form the molecular **layers** on both liquid and solid surfaces. A LB facility for film studies was setup and Cr8Cubane (aka $[Cr_8O_4(O_2CPh)_{16}] \bullet 5CH_2Cl_2$) was one of the first compounds used to test the formation of monomolecular layers on liquid surfaces. Below are Langmuir isotherms showing the ability to detect very weak hydrogen interactions as the molecules are compressed. The inset shows the primary molecular fragment without H atoms. The diameter of the molecular sphere of enclosure is 20.7Å.

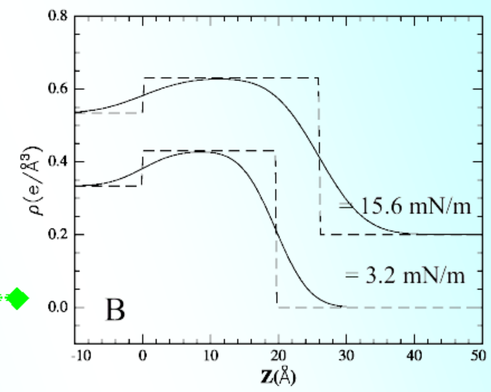


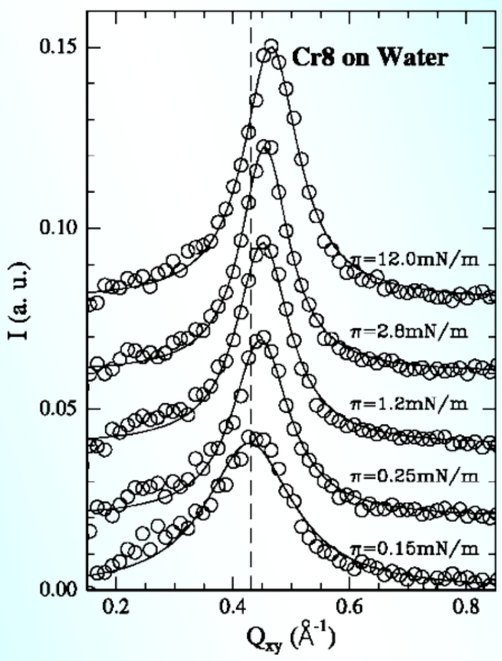
Material Synthesis → Physical Characterization → Traditional SSP Physics of the Bulk

Monolayers On Liquids → Physical Characterization

Molecules On Substrates → Physical Characterization → State of the Art Molecular Scale Physics

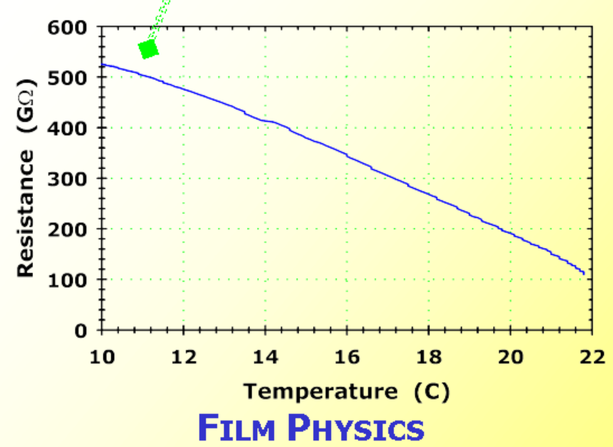
Molecules On Molecules → Physical Characterization → Near Future SupraMolecular Physics





Monolayer on Liquid Characterization

An important step in controlled monolayer formation is the study of the monolayer on the liquid surface. Top pane: measured electron density normal to the monolayer using **Surface X-ray Reflectivity** at two pressures. Bottom: **Grazing Incidence X-ray Diffraction** of the in plane 2D molecular ordering at various pressures. X-ray scattering work done in collaboration with David Vaknin (Ames Lab).



Film Physics

Exciting **electrical transport** result showing (semi)**conductivity** in a thin film where insulating behavior was predicted. Resistivity was measured across Al pads on glass substrate. R(glass)=2 PΩ, R(electrode gap)=13 TΩ, R_H=16 %, Vappl=100 V. Work done with the assistance of Joseph Shinar's group (Ames Lab).

Monolayer on Solids Characterization

Micron size monolayer regions were formed when the molecule Cr8Cubane was deposited on an etched silicon substrate. The **AFM** image shows the **<2 nm** high molecular **monolayer** on silicon. The 2D plot (5μm scale) shows a cross section of the film indicated on the lower image. AFM work done in collaboration with Hajime Takano and Marc Porter (Ames Lab).